ON THE PAIRING MECHANISM IN DOPED ARMCHAIR CARBON NANOTUBES

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Abstract

We review an electronic pairing mechanism driven by correlation, i.e. by the on-site repulsion; it works in a Hubbard model with the symmetry of the wrapped honeycomb lattice, suitable for single-wall \((N,N)\) carbon nanotubes. There is an important analogy with the one-band and three-bands Hubbard model for Cuprates: the Hubbard Hamiltonian for nanotubes also admits two-body singlet eigenstates with vanishing on-site repulsion, which we call \(W = 0\) pairs. By means of a non-perturbative canonical transformation we calculate the effective interaction between the electrons of a \(W = 0\) pair added to the interacting ground state. The interesting possibility of bound states is borne out by our approach provided the nanotube is doped away from half filling. Then, the dressed \(W = 0\) pair in the interacting many-body system is a bound state, and this occurs with quite reasonable parameter values. The pairing mechanism uses electronic degeneracy (or quasi-degeneracy) to produce attraction from repulsion. Pairing in Hubbard models has been reported by other authors as well, but the present approach has certain specific advantages. For example, it shows how pairing is favored by a large noncommutative symmetry Group (the Space Group, possibly supplemented by extra operations). This finding strongly suggests that the recently discovered superconductivity in carbon nanotubes could be at least partially due to an electronic mechanism; the physics involved could have some features in common with the case of High \(T_c\) compounds. From the effective interaction in the nanotubes we compute pair binding energies; we use exact diagonalization results for the \((1,1)\) nanotube to further confirm the analytic theory, then we consider the general trend. There is an optimal doping when the number of electrons per C atom is in the range 1.2–1.3. For \((N,N)\) nanotubes of length \(L\), the binding energy of the pair depends
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strongly on the filling and decreases towards a limiting value of the order of $0.1 \div 1$ meV as $L \to \infty$. We also present preliminary results on the inclusion of phonons in the present theory of pairing in the Hubbard model. Due to the need to include several oscillator branches the problem is hard and we resort to small cluster calculations, to start forming broad criteria. The results indicate that a strong Jahn-Teller effect induced by vector phonons may destroy the symmetry; the correlation-induced pairing, which is driven by the symmetry, is broken in such cases. However we also show examples where electronic and phonon-induced pairing are synergetic, both at weak coupling and in the polaronic regime, and the distortion is dynamically avoided.

1 Introduction

A single-wall carbon nanotube (SWNT)\[1\] is a graphite sheet wrapped onto a cylinder. The carbon atoms are arranged on the sites of a honeycomb lattice and the chirality of the wrapping determines the electronic properties of the tube. In particular the two main chiralities give rise to metallic (“armchair”) and semiconducting (“zig-zag”) SWNT’s. Metallic “armchair” tubes have four linear branches crossing the two Fermi points and the higher subbands, characterized by a nonvanishing transverse momentum, lie about $0.1 \sim 0.2$eV above. Therefore, in the very low-energy limit, they can be considered as strictly one dimensional systems. As a consequence there is general agreement in addressing their electronic properties to the Luttinger liquid class of universality\[2][3].

However such a low-energy scenario may be significantly changed if the nanotube is driven away from half filling, causing the instability of the Luttinger liquid fixed point. Indeed there has been growing evidence of superconducting fluctuations in SWNT’s placed between superconducting contacts\[4][5][6] up to the transition temperature of $\simeq 0.5$ K\[7].

It was also suggested that by a suitable injection of charge carriers, the density of states at the Fermi level may be increased, with a enhancement of the superconducting correlations. In a strongly doped regime the Fermi level is pushed away from the undoped position; as a consequence subbands with nonvanishing transverse momentum are involved in the low-energy scattering processes and a simple one dimensional description cannot be applied. In other terms, the transverse direction must be taken into account. The shift of the Fermi level can be achieved by two basic methods, i.e. by tuning an additional gate voltage or by intercalating alkali impurities. The electrochemical doping of ropes of carbon nanotubes has been reported in recent experiments\[8], where Litium was intercalated in the interstitial sites between the tubes arranged in a triangular lattice, up to a concentration corresponding to Li$_{1.7}$C$_6$. First principle calculations performed on this system showed that an almost complete charge transfer occurs between Li atoms and C atoms\[9]. Furthermore the resulting deformation of the nanotubes is predicted to be very small and as a consequence the transferred electrons mainly occupy the original bands of the carbon nanotubes. Finally the effect of doping consists on shifting the Fermi level about 1eV above the initial position and the electronic properties of the individual tubes result deeply modified.

Here we review an electronic pairing mechanism suitable for highly doped SWNT’s \[10][11]. We describe the tube with a Hubbard model defined on the wrapped honeycomb lattice, disregarding the long-range character of the Coulomb interaction. The long-range part of the interaction in nanotubes has been shown recently \[12] to have a marked influence
on the Coulomb blockade pattern, but can be safely disregarded here due to the small size of the pairs. The key point relies in identifying the Cooper pairs with the so called $W = 0$ pairs. A $W = 0$ pair is defined as an exact two-body singlet eigenstate of the Hubbard Hamiltonian without double occupancy. This means that a $W = 0$ pair is at the same time an eigenstate of the kinetic energy and of the Hubbard repulsion with vanishing eigenvalue for the latter.

$W = 0$ pairs arise in the presence of high enough symmetry, and provide a non-conventional mechanism of pairing from repulsive interactions in widely different materials. In recent years, we proposed a symmetry-driven configuration interaction pairing mechanism [13][14][15] in the two-dimensional (one-band and three-bands) repulsive Hubbard model for the Cuprates, showing that the $W = 0$ pairs, once dressed by the interaction, become bound states. Here, we wish to extend the approach in order to deal with the SWNT. We present analytic expressions for the effective interaction and obtain the binding energy for $(N,N)$ armchair nanotubes [see Fig.(1)]; in the case $N = 1$ we verify the analytic results by exact diagonalization and get high-precision agreement. Some experimental trends are correctly reproduced. In particular, a reasonable energy scale for the superconducting gap arises from the $\sim 1$eV input parameters and a stronger pairing is correctly predicted for smaller radii; this agrees with the measurements in SWNT by Tang et al.[5].

We get effective attraction and pairing for doped nanotubes, and starting from the undoped system we find that the pair binding energy grows as the number of electrons per C atom increases until an optimum is reached.

## 2 $W = 0$ Pairs in the Hubbard Model

The Hubbard Hamiltonian $H$ on the wrapped honeycomb lattice for the valence bands of $(N,N)$ SWNT’s reads:

$$H = H_0 + W = t \sum_{\langle \mathbf{r}, \mathbf{r}' \rangle} \sum_{\sigma} (c_{\mathbf{r}, \sigma}^\dagger c_{\mathbf{r}', \sigma} + h.c.) + U \sum_{\mathbf{r}} \hat{n}_{\mathbf{r}, \uparrow} \hat{n}_{\mathbf{r}, \downarrow},$$

(1)
where \( \mathbf{r} \) denotes the honeycomb site, the sum runs over the pairs \( \langle \mathbf{r}, \mathbf{r}' \rangle \) of nearest neighbour carbon atoms, \( t \) is the hopping parameter and \( U \) is the on-site Hubbard repulsion. The one-body eigenvalues \( \varepsilon^\pm(k) \), (- for the bonding and + for the antibonding bands) are readily obtained[10], and the Fermi line has \( C_{2v} \) symmetry for the nanotubes (\( C_{6v} \) for the graphite sheet). Here, we assume that the Fermi level \( \varepsilon_F \) lies in the + band as for alkali-doped compounds.

The particles forming a \( W = 0 \) pair have no direct interaction and are the most natural candidates to achieve bound states in purely repulsive Hubbard models. We note that such states are also building bricks of the ground state of Hubbard and related models at half filling[16][17][18]. Recently we obtained[15][19] a general criterion to get all the \( W = 0 \) pairs for Hubbard models defined on any graph. In the case of triplet pairs the absence of the on-site interaction in the Hubbard model is a trivial consequence of the Pauli principle; the point that we wish to make here is that the extension to singlet eigenstates of the Hamiltonian can only be a consequence of symmetry and is possible only when enough symmetry is present. When such solutions exist, we can fully classify them and predict their properties by the use of Group theory. The square or hexagonal point symmetry is not generally enough. We must speak in terms of the Optimal Group \( \mathcal{G}_0 \) of the Hamiltonian, that we define as a symmetry Group that has enough operations to justify the degeneracy of the single particle energy levels. We have relegated all the technicalities in the next subsection, which may be skipped by those readers who are unfamiliar with Group Theory or are satisfied with an intuitive understanding of the argument; for those readers, the essence of the next Subsection is that \( W = 0 \) pairs belong to well defined symmetry types, that are completely different from those where single particle solutions of the same Hamiltonians exist. The theorem also tells us that the bigger is \( \mathcal{G}_0 \), the larger is the number of \( W = 0 \) pairs.

### 2.1 A Useful Theorem

Let \( \mathcal{G}_0 \) be the the symmetry Group of the non-interacting Hubbard Hamiltonian \( K = \sum_{\langle ij \rangle, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} \) defined on an arbitrary graph \( \Lambda \). By definition no degeneracy between one-body eigenstates is accidental, hence \( \mathcal{G}_0 \) must contain enough operations to justify all such degeneracies. Let us label each one-body eigenstate of \( H = K + W \), \( W = \sum_{i \in \Lambda} U_i n_i^{\uparrow} n_i^{\downarrow} \), with an irreducible representation (irrep) of \( \mathcal{G}_0 \).

**Definition.** An irrep \( \eta \) is represented in the one-body spectrum of \( H \) if at least one of the one-body levels belongs to \( \eta \).

Let \( \mathcal{E} \) be the set of the irreps of \( \mathcal{G}_0 \) which are represented in the one-body spectrum of \( H \). Let \( |\psi\rangle \) be a two-body eigenstate of the non-interacting Hamiltonian with spin \( S_z = 0 \) and \( P^{\eta} \) the projection operator on the irrep \( \eta \).

We wish to prove the

**\( W = 0 \) Theorem.** Any nonvanishing projection of \( |\psi\rangle \) on an irrep not contained in \( \mathcal{E} \), is an eigenstate of \( H \) with no double occupancy. The singlet component of this state is a \( W = 0 \) pair. Conversely, any pair belonging to an irrep represented in the spectrum must have non-vanishing \( W \) expectation value:
that this condition is satisfied if and only if 

\[ P \not\in \sigma \Leftrightarrow WP^{(n)}|\psi\rangle = 0. \quad (2) \]

**Remark:** Suppose we perform a gauge change in \( H \) such that \( \sigma_0 \) is preserved; clearly, a \( W = 0 \) pair goes to another \( W = 0 \) pair. Thus, the theorem implies a distinction between symmetry types which is gauge-independent.

**Proof:** Let us consider a two-body state of opposite spins belonging to the irrep \( \eta \) of \( \sigma_0 \):

\[ |\psi^{(n)}\rangle = \sum_{i \in \Lambda} \psi^{(n)}(i, i) c_i^\dagger c_i^\dagger |0\rangle. \]

Then we have

\[ n_i n_{\bar{i}} |\psi^{(n)}\rangle = \psi^{(n)}(i, i) c_i^\dagger c_i^\dagger |0\rangle \equiv \psi^{(n)}(i, i) |i \uparrow, i \downarrow\rangle. \]

We define \( P^{(n)} \) as the projection operator on the irrep \( \eta \). By definition

\[ P^{(n)} \sum_{i \in \Lambda} \psi^{(n)}(i, i) |i \uparrow, i \downarrow\rangle = \sum_{i \in \Lambda} \psi^{(n)}(i, i) |i \uparrow, i \downarrow\rangle, \]

and therefore \( \psi^{(n)}(i, i) = 0, \forall i \in \Lambda \), provided \( P^{(n)} |i \uparrow, i \downarrow\rangle = 0, \forall i \in \Lambda \). It is worth noting that this condition is satisfied if and only if \( P^{(n)} |i \sigma\rangle = 0 \), \( \forall i \in \Lambda \), where \( |i \sigma\rangle = c_i^\dagger |0\rangle \). Now it is always possible to write \( |i \sigma\rangle \) in the form \( |i \sigma\rangle = \sum_{\eta \in \varepsilon} c^{(n)}(i) |\eta_{\varepsilon}\rangle \) where \( |\eta_{\varepsilon}\rangle \) is the one-body eigenstate of \( H \) with spin \( \sigma \) belonging to the irrep \( \eta \). Hence, if \( \eta \not\in \varepsilon \), \( P^{(n)} |i \sigma\rangle \) vanishes and so does \( P^{(n)} |i \uparrow, i \downarrow\rangle \). Therefore, if \( |\psi^{(n)}\rangle \) is a two-hole singlet eigenstate of the kinetic term and \( \eta \not\in \varepsilon \), then it is also an eigenstate of \( W \) with vanishing eigenvalue, that is a \( W = 0 \) pair.

Q.E.D.  

As anticipated above, the theorem also tells us that the bigger is \( \sigma_0 \), the larger is the number of \( W = 0 \) pairs. Indeed, for a given system, the number of one-body eigenvectors is fixed, while the number and the dimension of the irreps grow with the order of the group. Therefore, also the number of irreps not represented in \( \varepsilon \) grows, meaning more \( W = 0 \) pairs.

Moreover a partial use of this theorem is possible if we know only a subgroup \( G_0 \subset \sigma_0 \). In this case the \("\Rightarrow\"\) implication still holds for the irreps of \( G_0 \).

### 2.2 Symmetry of \( W = 0 \) Pairs for Carbon Nanotubes

For the \((N, N)\) SWNT, we used the Space Group as \( G_0 \). We considered the case \( N > 1 \) and we focused on the subspace of vanishing quasi-momentum. We found that the only \( W = 0 \) pairs belong to the pseudoscalar irrep \( A_2 \). Let \((a, b)\) denote the basis of the Bravais lattice [see Fig.(1)] and \( u(k, \zeta) \) the periodic part of the Bloch function of quasi-momentum \( k \), with \( \zeta = a, b \). The pair wavefunction reads[10]

\[
\psi^{[A_2]}_{\zeta_1, \zeta_2}(k, R_1, R_2) = \sin(k_x(X_1 - X_2)) \times \frac{1}{\sqrt{2}} \left[ u^*(k, \zeta_1) u^*(-k, \zeta_2) e^{ik_y(Y_1 - Y_2)} - u^*(k, \zeta_2) u^*(-k, \zeta_1) e^{-ik_y(Y_1 - Y_2)} \right] \chi_0, \quad (3)
\]

where the origin of the cell has been denoted with the capital \( R = (X, Y) \); \( \chi_0 \) is the singlet spin function. We can verify by direct inspection that \( \psi^{[A_2]}_{\zeta_1, \zeta_2}(k, R_1, R_2) \) vanishes for \( X_1 = X_2 \),...
that is the two-body singlet wavefunction vanishes if the particles lie on the same annulus of the \((N,N)\) tube. As a consequence \(\psi_{\xi_1,\xi_2}^{[A_2]}(k,\mathbf{R}_1,\mathbf{R}_2)\) is an eigenstate of the kinetic energy \(H_0\) [with eigenvalue \(2\varepsilon(k)\)] and of the on-site Hubbard repulsion \(W\) with vanishing eigenvalue of the latter, that is \(\psi_{\xi_1,\xi_2}^{[A_2]}(k,\mathbf{R}_1,\mathbf{R}_2)\) is a \(W=0\) pair. The wave-function \(\psi^{[A_2]}\) vanishes when the transverse component \(k_y=0\).

3 \(W=0\) Pairing: General Theory

In this Section we present our proposal for an electronic pairing mechanism. Looking at the experimental data we also argue that our description contains much of the essential physics. One of the distinct advantages of our approach over some competitors in the literature is that it lends itself to detailed comparison between the theory and the exact numerical data from clusters. The size of the clusters can be so small that we can comfortably afford exact calculations, but the choice of the geometry is important to ensure that the symmetry based theoretical formulation applies directly without misleading complications. Next, we show how this philosophy applies, using data from a tiny SWNT model and those from a square CuO\(_4\) cluster in parallel. The latter geometry is relevant to Cu-O planes, and the way pairing is produced is similar. So we may claim that the \(W=0\) mechanism has enough universal character to be relevant in principle at least to other case besides SWNT.

We must define an appropriate effective interaction among the electrons of a \(W=0\) pair added to the \(n\)-body interacting ground state \(|\Psi_0(n)\rangle\). Although the two extra particles cannot interact directly by definition of \(W=0\) pair, they can virtually exchange electron-hole excitations. To the extent that electron-hole excitations behave like Bose particles, they can act as the phonons do in the Fröhlich interaction. Incidentally, this is what all the electronic mechanisms of pairing on the market aim to do, but we place special emphasis on the role of symmetry, degeneracy and our special pairs.

Many configurations contribute to the interacting \((n+2)\)-body ground state \(|\Psi_0(n+2)\rangle\) and we need a complete set \(s\) to expand it exactly; as long as it is complete, however, we can design \(s\) as we please. We can take the non-interacting \(n\)-body Fermi sphere \(|\Phi_0(n)\rangle\) as our vacuum and build the complete set in terms of excitations over it. In the subspace with vanishing spin \(z\) component, the simplest states that enter the configuration mixing are those obtained from \(|\Phi_0(n)\rangle\) by creating two extra electrons over it; we denote with \(|m\rangle\) these states. Similarly, along with the pair \(m\) states, we introduce the 4-body \(\alpha\) states, obtained from \(|\Phi_0(n)\rangle\) by creating 2 electrons and 1 electron-hole (e-h) pair. Then \(s\) includes the 6-body \(\beta\) states having 2 electrons and 2 e-h pairs, and so on. We are using Greek indices for the configurations containing the electron-hole pairs, which here are playing largely the same rôle as phonons in the Cooper theory. By means of the complete set \(s\) we now expand the interacting ground state

\[
|\Psi_0(n+2)\rangle = \sum_m a_m |m\rangle + \sum_\alpha a_\alpha |\alpha\rangle + \sum_\beta a_\beta |\beta\rangle + \ldots \tag{4}
\]

and set up the Schrödinger equation

\[
H|\Psi_0(n+2)\rangle = E(n+2)|\Psi_0(n+2)\rangle. \tag{5}
\]
We stress that Eq.(4) is configuration interaction, not a perturbative expansion. When the number $n$ of electrons in the system is such that $|\Phi_0(n)\rangle$ is a single non-degenerate determinant (the Fermi surface is totally filled), we can easily and unambiguously define and calculate the effective interaction between the two extra electrons since the expansion in Eq.(4) for the interacting ground state is unique: this is done by a canonical transformation[14],[20],[21] from the many-body Hamiltonian of Eq.(1). We consider the effects of the operators $H_0$ and $W$ on the terms of $|\Psi_0(n+2)\rangle$. Choosing the $m, \alpha, \beta, \ldots$ states to be eigenstates of the kinetic energy $H_0$ we have

$$H_0|m\rangle = E_m|m\rangle, \quad H_0|\alpha\rangle = E_\alpha|\alpha\rangle, \quad H_0|\beta\rangle = E_\beta|\beta\rangle, \quad \ldots.$$  

(6)

Since $W$ can create or destroy up to 2 e-h pairs, its action on an $m$ state yields

$$W|m\rangle = \sum_{m'} W_{m',m}|m'\rangle + \sum_\alpha W_{\alpha,m}|\alpha\rangle + \sum_\beta W_{\beta,m}|\beta\rangle.$$  

(7)

The action of $W$ on the $\alpha$ states yields

$$W|\alpha\rangle = \sum_m W_{m,\alpha}|m\rangle + \sum_{\alpha'} W_{\alpha',\alpha}|\alpha'\rangle + \sum_\beta W_{\beta,\alpha}|\beta\rangle + \sum_\gamma W_{\gamma,\alpha}|\gamma\rangle.$$  

(8)

where scattering between 4-body states is allowed by the second term, and so on. In this way we obtain an algebraic system for the coefficients of the configuration interaction of Eq.(4). However to test the instability of the Fermi liquid towards pairing it is sufficient to study the amplitudes $a_m$ of the $m$ states. In the weak coupling limit this can be done by truncating the expansion in Eq.(4) to the $\alpha$ states because, as we have shown[20], the inclusion of the $\beta, \gamma, \ldots$ states produces a $E$-dependent renormalization of the matrix elements of higher order in $W$, leaving the structure of the equations unaltered.

By taking a linear combination of the $\alpha$ states in such a way that

$$(H_0 + W)_{\alpha,\alpha'} = \delta_{\alpha\alpha'} E_{\alpha}$$

(9)

the algebraic system reduces to

$$[E_m - E(n+2)]a_m + \sum_{m'} a_{m'} W_{m,m'} + \sum_\alpha a_\alpha W_{\alpha,m} = 0$$  

(10)

$$[E_{\alpha'} - E(n+2)]a_{\alpha} + \sum_{m'} a_{m'} W_{\alpha,m'} = 0.$$  

(11)

Solving for $a_\alpha$ and substituting in Eq.(10) we exactly decouple the 4-body states as well, ending up with an equation for the dressed pair $|\psi\rangle = \sum_m a_m|m\rangle$. The effective Schrödinger equation for the pair reads

$$(H_0 + W + S[E])|\psi\rangle \equiv H_{\text{pair}}|\psi\rangle = E|\psi\rangle$$  

(12)

where

$$(S[E])_{m,m'} = -\sum_\alpha \frac{W_{m,\alpha} W_{\alpha,m'}}{E_\alpha - E}.$$  

(13)
is the scattering operator. The matrix elements $W_{m,m'}$ in Eq.(12) may be written as the sum of two terms representing the direct interaction $W_{m,m'}^{(d)}$ among the particles forming the pair and the first-order self-energy $W_{m}$:

$$W_{m,m'} = W_{m,m'}^{(d)} + \delta_{m,m'} W_{m}.$$  (14)

Analogously in $S[E]$ we may recognize two different contributions; one is the true effective interaction $W_{\text{eff}}$ between the electrons of the $m$ states, while the other one is the forward scattering term $F$

$$S_{m,m'} = (W_{\text{eff}})_{m,m'} + F_{m} \delta_{m,m'}.$$  (15)

The first-order self-energy and the forward scattering term are diagonal in the indices $m$ and $m'$. $W_{m}$ and $F_{m}$ renormalize the non-interacting energy $E_{m}$ of the $m$ states:

$$E_{m} \rightarrow E_{m}^{(R)} = E_{m} + W_{m} + F_{m}.$$  (16)

Eq.(12) is of the form of a Schrödinger equation with eigenvalue $E(n+2)$ for the added pair with the interaction $W^{(d)} + W_{\text{eff}}$. Here the $W = 0$ pairs are special because $W^{(d)}$ vanishes. We interpret $a_{m}$ as the wave function of the dressed pair, which is acted upon by an effective Hamiltonian $H_{\text{pair}}$. This way of looking at Eq.(12) is perfectly consistent, despite the presence of the many-body eigenvalue $E(n+2)$. Indeed, if the interaction is attractive and produces bound states the spectrum of Eq.(12) contains discrete states below the threshold of the continuum (two-electron Fermi energy). This is a clear-cut criterion for pairing, which is exact in principle. The threshold is given by

$$E_{F}^{(R)} \equiv \min_{\{m\}} \left[ E_{m}^{(R)}(E) \right],$$  (17)

which contains all the pairwise interactions except those between the particles in the pair; it must be determined once Eq.(12) has been solved (since $F$ depends on the solution). The ground state energy $E$ may be conveniently written as $E_{F}^{(R)} + \Delta$. $\Delta < 0$ indicates a Cooper-like instability of the normal Fermi liquid and its magnitude represents the binding energy of the pair.

We emphasize that in principle the canonical transformation is exact because in this way our framework does not require $U/t$ to be small. The next problem is how to find a practical estimate of the renormalized Fermi energy. In the numerical calculations, some approximation is needed. In Sections 4 and 5, we shall compute the bare quantities; that is, we shall neglect the 6-body and higher excitations in the calculation of $W_{\text{eff}}$ and $F$. This is a good approximation if the corrections to the Fermi liquid background are small and the exact numerical results on symmetric clusters suggest that this is the case, see next Section; the canonical transformation can be pushed to include more terms if necessary.

We want to stress that once the expansion of $|\Psi_{0}(n+2)\rangle$ in Eq.(4) is truncated as specified above we do not need to construct a good approximation of the interacting ground state wave function in order to get the $a_{m}$ amplitudes at weak coupling; in this way we obtain information about pairing.

We conclude this Section by stressing that the Hubbard model is an instructive oversimplification of reality. Therefore it would be appropriate to include the effects of phonons
within the theory described above. In this case, the $W = 0$ mechanism could still be very important as a way to get rid of the huge on-site repulsion; but then it could be unable to provide enough binding energy without allies. This scenario will be investigated in Section 4.1.

4 Results on Symmetric Clusters: Carbon Nanotubes vs Cuprates

The canonical transformation outlined above is completely general and can be readily applied to any system having enough symmetry for $W = 0$ pairs to occur. In this Section we show that $W = 0$ pairing realizes both in hexagonal and square systems, suggesting that superconductivity in the wrapped graphite sheets of carbon nanotubes and in the Cu-O planes of cuprates can in principle have a common origin.

We shall consider two prototype clusters, namely the the $(1,1)$ tube of length $L = 2$ (in units of the lattice spacing) and periodic boundary conditions and the CuO$_4$ plaquette, see Fig.(2). These systems are the smallest ones with the appropriate symmetry showing the superconducting $W = 0$ pairing. Therefore, they represent a very good probe to test the pairing mechanism shown in previous Section, since we can compare exact diagonalization results with the analytic approximations of the canonical transformation.

We define, following Refs.[22][23],

$$\tilde{\Delta}(N + 2) = E(N + 2) + E(N) - 2E(N + 1), \quad (18)$$

where $E(N)$ is the ground state energy with $N$ electrons (holes for Cuprates) referenced to the electron vacuum. $|\tilde{\Delta}(N + 2)|$ is one definition of the pairing energy. This definition is simple, but requires computing the eigenvalues with great accuracy, and has several drawbacks. It says nothing about the dynamics which leads to pairing. Moreover, generally a negative $\tilde{\Delta}$ does not unambiguously imply pairing, and further problems arise since the above definition depends on the comparison of systems with different $N$. However, in several studies of $W = 0$ pairing in finite systems when it was possible to compute $\tilde{\Delta}$ by exact diagonalization we pointed out[13][15][21] that at least at weak coupling it agrees well with $\Delta$ as obtained by the canonical transformation. This supports the application of Eq.(18).

Below we compute the interacting ground state energy with 2, 3 and 4 particles by exact numerical diagonalization in order to get $\tilde{\Delta}(4)$ for the $(1,1)$ nanotube and for the CuO$_4$ cluster. Finally the canonical transformation is applied to evaluate $\Delta(4)$ which will be compared with $\tilde{\Delta}(4)$.

For the clusters depicted in Fig.(2), we have determined the Optimal Group[10][24] and found that the low energy one-body spectrum consists of a non-degenerate fundamental level and a threefold degenerate first-excited one. By applying the Theorem in Section 2.1, $W = 0$ pairs were found in both clusters and hence the possibility of negative $\Delta$ and $\tilde{\Delta}$ can be investigated.

In the non-interacting limit the ground state with 4 fermions is obtained by adding a $W = 0$ pair to the Fermi sphere, i.e. the non-interacting ground state with two fermions. In Fig.(3) $\tilde{\Delta}(4)$ is reported for the two cases and it is negative for a large range of the ratio.
(a) The Hubbard Model of the (1,1) nanotube of length $L = 2$ (in units of the lattice spacing) and periodic boundary conditions; the dashed lines denote hopping interactions due to the wrapping. (b) CuO$_4$ cluster.

$U/t$. In this range the effective interaction between the particles of the added $W = 0$ pair is attractive. The similarity of the curves in Fig.(3) suggests that the paring mechanism in the two prototype systems is actually the same. Hence, the (1,1) tube results to be a very good probe to test the canonical transformation for armchair carbon nanotubes as the CuO$_4$ is for Cuprates.

Figure 3: Trend of $\tilde{\Delta}(4)$ versus Log $U$ in the range -1 ÷ 3 (a) for the (1,1) nanotube and (b) for the CuO$_4$. Energies are in unit of $t$.

The analytic canonical transformation can be readily done and the results are shown in Fig.(4). The agreement between $\tilde{\Delta}(4)$ and $\Delta$ is again very good. The ratio of the second derivatives with respect to $U/t$ at $U = 0$ was estimated by using best fits and turned out to be 1.00003, while the first derivative vanishes. The binding energy for $U < t$ is in the meV range.

4.1 $W = 0$ Pairing and Electron-Phonon Interactions

Many high-$T_C$ compounds exhibit a measurable isotope effect, which depends on doping. This experimental fact, the partly ionic nature of the oxides, and the existence of phonon frequencies in the same range as the pair binding energy suggests that Electron-Phonon (EP) interactions could be important and should be included in the theory. In particular there is experimental evidence that the half breathing Cu-O bond stretching mode at
k = (π, 0), (0, π) is significantly coupled with the doped holes in the superconducting regime and its contribution may be relevant for the \( d_{x^2−y^2} \) pairing[25]. Even the Hubbard model for the SWNT can be questioned on similar grounds. In the conventional BCS mechanism, phonons overscreen the electron repulsion; what happens if electronic screening already leads to pairing? It is not obvious that the phonons will reinforce the attraction while preserving the symmetry. More generally, some vibrations could favour the pairing and others could be pair-breaking. This poses a special, conceptual difficulty for the present mechanism since any distortion of the lattice can be fatal to the \( W = 0 \) pairs.

Therefore, we address the general question if the \( W = 0 \) pairing available in the Hubbard model survives when the lattice degrees of freedom are taken into account. We use an extension of the Hubbard model in which bond stretchings dictate the couplings to the normal modes of the \( C_{4v} \)-symmetric configuration. In this way a long-range (Fröhlich) EP interaction arises.

Consider the Hubbard model appropriate for the Cu-O plane with on-site interaction \( U \). We expand the hopping integrals \( t(r_i, r_j) \) in powers of the displacements \( \rho_i \) around a \( C_{4v} \)-symmetric equilibrium configuration

\[
t(r_i, r_j) ≃ t^0(r_i, r_j) + \sum_\alpha \left[ \frac{\partial t(r_i, r_j)}{\partial r_i^\alpha} \right]_0 \rho_i^\alpha + \sum_\alpha \left[ \frac{\partial t(r_i, r_j)}{\partial r_j^\alpha} \right]_0 \rho_j^\alpha,
\]

where \( \alpha = x, y \). Below, we write down the \( \rho_i^\alpha \) in terms of the normal modes \( q_\eta^\nu \): \( \rho_i^\alpha = \sum_\eta \phi_\eta^\alpha(i) q_\eta^\nu \), where \( \eta \) is the label of an irreducible representation of the symmetry group of the undistorted system and \( \nu \) is a phonon branch.

The Cu atoms is fixed, for the sake of simplicity; the electron-lattice Hamiltonian reads:

\[
H_{el−latt} = H_0 + V_{tot},
\]

where \( H_0 = H_0^a + H_0^\sigma \) accounts for the kinetic part of the electron-phonon system. We have

\[
H_0 = \sum_\eta \hbar \omega_\eta^\nu b_\eta^\nu b_\eta^\dagger + \sum_{i,j,\sigma} t^0_i(r_i, r_j) c_i^\dagger \sigma c_j^\sigma,
\]
where the $\omega$’s are normal mode frequencies. The interacting part $V_{\text{tot}} = V + W$ contains the Hubbard repulsion $W$ and the electron-phonon interaction $V$. The latter can be written in terms of the parameters $\xi_{\eta,\nu} = \lambda_{\eta,\nu} \sqrt{\frac{\hbar \omega_{\eta,\nu}}{2 M_{\eta,\nu}}}$, where the $\lambda$’s are numbers of order unity that modulate the EP coupling strength, while $M$ is the Oxygen mass. Then,

$$V = \sum_{\eta,\nu} \xi_{\eta,\nu} (b_{\eta,\nu}^{\dagger} + b_{\eta,\nu}) H_{\eta,\nu},$$

and the $H_{\eta,\nu}$ operators are given by

$$H_{\eta,\nu} = \sum_{i,j} \sum_{\alpha,\sigma} \left\{ s_{\eta,\nu}^{\alpha}(i) \left[ \frac{\partial f_{\alpha}(r_i, r_{\nu})}{\partial r_{\alpha} i} \right] 0 + s_{\eta,\nu}^{\alpha}(j) \left[ \frac{\partial f_{\alpha}(r_{\nu}, r_j)}{\partial r_{\alpha} j} \right] 0 \right\} (c_{i,\alpha}^{\dagger} c_{j,\sigma} + h.c.).$$

This is physically more detailed than the Hubbard-Holstein model, where electrons are coupled to a local Einstein phonon and the superconducting phase has been investigated in detail[26],[27]. Indeed, in the present context the Hubbard-Holstein model is not fully satisfactory because it restricts to on-site EP couplings, which would be impaired by a strong Hubbard repulsion. On the other hand the use of a Fröhlich-like phonons was suggested[28],[29],[30] for modeling the Cu-O planes in the strong EP coupling regime: a long-range EP coupling removes the problem of polaron self-trapping, otherwise present in the case of the Holstein interaction, where an unphysically large polaron (and bipolaron) mass occurs.

By generalizing to $H_{\text{el-latt}}$ the canonical transformation proposed for the electronic part $H = H_{\text{el}}^0 + W$, one can derive[31],[32] an effective interaction between the particles in the pair. We obtained a new Cooper-like equation $H_{\text{pair}}(\phi) = E(\phi)$ with an effective two-body Hamiltonian, acting upon the dressed $W = 0$ pair $|\phi\rangle$. As in Section 3 the pairing criterion involves the properly renormalized Fermi energy $E_F^{(R)}$: if the lowest energy eigenvalue $E$ is such that $E = E_F^{(R)} + \Delta$ with negative $\Delta$, the dressed $W = 0$ pair gets bound in the many-body interacting problem and the system undergoes a Cooper instability. We observed that this extended approach is very accurate at weak coupling and is qualitatively predictive also in the intermediate coupling regime.

The numerical calculations were done on CuO$_4$, which yields $\tilde{\Delta}(4) < 0$. The cluster CuO$_4$ is actually so small that it allows only the coupling to phonons at the centre or at the edge of the Brillouin Zone. Fortunately, however, phonons near the edge are precisely the most important ones for this system[25]. A standard Jahn-Teller calculation in which the degenerate ground state wave functions interact with the vibrations predicts distortions that already at moderate Electron-Phonon coupling destroy the pairing[32]. We also explored the scenario beyond this approximation. We have solved analytically the Cooper-like equation and found instead that the phonons help the electronic pairing to occur.

We resorted to exact numerical solutions in order to go beyond the weak-coupling regime, although we still used mild enough couplings to achieve the convergence with few excitations per mode. It turned out that the catastrophic distortions predicted by the Jahn-Teller approximation are an artifact, and that one needs a a broader spectrum of electronic states than is usually considered to get the correct answer. We could also explore the strong coupling regime by discarding the less influential modes and by including many excitations for the relevant modes. Interestingly, in the symmetry channels where $W = 0$
pairs occur, pairing may survive. We praise the fact that the numerics validate the results of
the analytical canonical transformation. The analytical calculation also correctly predicts
which normal modes are pair-hailing and which are pair-breaking. In summary, our find-
ings suggest a joint mechanism, with the Hubbard model that captures a crucial part of the
physics.

5 Pairing in Doped Carbon Nanotubes

The results of the previous Section encourage us to proceed with larger and more physical
systems than the (1,1) SWNT. In this Section we calculate the effective interaction [whose
diagrammatic expansion is depicted in Fig.(5)] between the electrons of the W \(= 0\) pair
described by Eq.(3) in \((N,N)\) nanotubes of length \(L\) with \(4 < N < 16\) and \(10 < L < 32\) (in
units of the lattice spacing).

Following the general theory described in Section 3, we calculate the quantities entering
the Cooper Equation (12). Letting \(n^{(0)}(p)\) denote the non-interacting occupation number in
band \(\nu\) with wavevector \(p\), we find

\[
W_{\text{eff}}(k,k',E) = 2 \sum_{\hat{O} \in C_2} \chi^{(A_2)}(\hat{O}) \sum_{p,\nu} [1 - n^{(0)}_+ (\hat{O}k' + k + p)] n^{(0)}_{\nu}(p) \times \\
\times \frac{U_{\nu}(\hat{O}k' + k + p, -k, \hat{O}k', p) U_{\nu}(k, p, \hat{O}k' + k + p, -\hat{O}k')}{\varepsilon^+(\hat{O}k' + k + p) - \varepsilon^\nu(p) + \varepsilon^+(k') + \varepsilon^+(k) - E}
\]

(19)

where \(\chi^{(\eta)}(\hat{O})\) is the character in \(\eta\) of the operation \(\hat{O}\) of \(C_2\), \(E\) is the interacting pair energy
and \(U_{\nu}(k_1, k_2, k_3, k_4)\) is the interaction vertex, with incoming legs \(k_3\) and \(k_4\) in band + and
outgoing \(k_1\) in band + and \(k_2\) legs in band \(\nu\). The effective Schrödinger equation for the
pair reads

\[
[2\varepsilon(k) + W_F + F(k,E)] a_k + \sum_{k' \in D/4} W_{\text{eff}}(k, k', E) a_{k'} = E a_k ,
\]

(20)

where \(W_F\) is the \(k\)-independent first-order self-energy shift [see Eq.(14)] given by

\[
W_F = U \left[ 2 \left( \frac{n/2}{4NL} \right)^2 + \frac{n/2}{4N^2L^2} \right]
\]

(21)

and

\[
F(k, k', E) = -2\delta(k - k') \times
\]
Table 1: Pair binding energy $-\Delta$ (meV) and Average Effective Interaction $V$ (eV) for $(N,N)$ nanotubes of various lengths $L$, as a function of the Fermi energy $\varepsilon_F$. Numerical values were computed with $t = 1$ eV and $U = 1.7$ eV for illustration.

<table>
<thead>
<tr>
<th>$L$</th>
<th>$N = 2$</th>
<th>$N = 4$</th>
<th>$N = 6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$\varepsilon_F$</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>$-\Delta$</td>
<td>12.2</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>$\nu$</td>
<td>0.54</td>
<td>0.43</td>
</tr>
<tr>
<td>20</td>
<td>$\varepsilon_F$</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>$-\Delta$</td>
<td>5.7</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>$\nu$</td>
<td>0.38</td>
<td>0.41</td>
</tr>
<tr>
<td>32</td>
<td>$\varepsilon_F$</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>$-\Delta$</td>
<td>3.6</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>$\nu$</td>
<td>0.35</td>
<td>0.36</td>
</tr>
</tbody>
</table>

\[
\sum_{\nu} \sum_{q} \left[ 1 - n_{\nu}^{(0)}(k + p - q) \right] \left[ 1 - n_{\nu}^{(0)}(q) \right] \frac{n_{\nu}^{(0)}(p)}{E_{\nu}(k + p + q) - E_{\nu}(k) + E_{\nu}(p) + E_{\nu}(q) + E_{\nu}(p) - E} |U_{\nu}(k, p, k + p - q, q)|^2
\]  

is the forward scattering term which does not contains any direct interaction between the particles of the pair. Eq.(20) requires a self-consistent calculation of $E$ (since $W_{\text{eff}}$ and $F$ are $E$-dependent). The indices $k$ and $k'$ run over $1/4$ of the empty part of the First Brillouin Zone and we denoted such a set of wavevectors as $\Phi/4$. We show below that $E = 2\varepsilon_F + W_F + F_{\text{min}} + \Delta$, with $\Delta < 0$ which implies a positive binding energy $-\Delta$ of the $W = 0$ pair; here $F_{\text{min}}$ is the minimum value of $F(k,E)$ among the wavevectors $k$ on the Fermi line.

We solved the Cooper-like equation (20) in a virtually exact way using the hopping parameter $t = 1$ eV and $U/t = 1.7$ (which is of the correct order of magnitude for graphite [33][34]). The calculations are performed with the Fermi energy $\varepsilon_F$ varying between 0.5 eV and 1.2 eV (half filling corresponds to $\varepsilon_F = 0$). As in the (1,1) cluster, the $W = 0$ singlets show pairing, albeit in general in $^1A_2$, see Table I. The binding energy $-\Delta$ of the pairs decreases monotonically both with the radius and the length of the tube.

Figure 6: Results of the canonical transformation approach with $t = 1$ eV and $U = 1.7$ eV. (a) $-\Delta_{\text{asympt}}$ (eV) as a function of the Fermi energy $\varepsilon_F$ for $N = 4$ (empty triangles), $N = 8$ (black boxes) and $N = 16$ (grey diamonds). The Fermi energy varies in the range $0.6 \div 1.2$ eV. (b) $-\Delta_{\text{asympt}}$ (eV) as a function of $N$ for $N$ in the range $4 \div 36$ and $\varepsilon_F = 1$ eV.
With supercell sizes \( N_C = 2N \times L > 400 \) numerical calculations become hard. Since we are concerned with the asymptotic behaviour for fixed \( N \) and \( L \rightarrow \infty \) and \( \Delta(N, L) \) depends on \( N \) and \( L \) in a complicated way, we need a method to make reliable extrapolations of the numerical results. To this end, like in previous work\[14]\,[35] we define the Average Effective Interaction \( V \). This is such that setting in Eq.(20) \( W_{\text{eff}} = \frac{V}{N_C} \), with a constant \( V > 0 \) for all \( k \) and \( k' \) in \( D/4 \), one obtains the correct value of \( \Delta \), i.e., the same as obtained by solving Eq. (20) with \( W_{\text{eff}}(k, k') \). In other terms, once the binding energy \( -\Delta(N, L) \) is known, the constant \( V \) must be chosen in such a way that

\[
\frac{1}{V} = \frac{1}{N_C} \sum_{k \in D/4} \frac{1}{2\epsilon(k) + F(k)} - \frac{1}{2\epsilon_F + F_{\text{min}}(k_F)} - \Delta(N, L).
\]  

In Table I we report the value of \( V \) which remains fairly stable around \( \approx 0.4 \) eV with increasing \( L \). Therefore \( V \) must be interpreted as a characteristic energy scale of the system which is largely independent of the Fermi energy and of the radius. This allows us to extrapolate to \( \Delta_{\text{asympt}}(N) = \lim_{L \rightarrow \infty} \Delta(N, L) \). Solving Eq.(23) with \( V \approx 0.4 \) eV for \( L \rightarrow \infty \) the new unknown \( \Delta_{\text{asympt}}(N) \) can be obtained numerically. We did so for several values of \( N \) and \( \epsilon_F \) and found that \( \Delta_{\text{asympt}} \) is strongly dependent on the filling at fixed \( N \), as illustrated in Fig.(6.a). The sharp maximum at the optimal doping \( \epsilon_F \approx 1 \) can be understood in terms of a corresponding peak in the density of states; we observe that \( -\Delta_{\text{asympt}}(N) \) decreases monotonically as the radius of the tube increases [see Fig.(6.b)] i.e. a higher critical Temperature is predicted for smaller nanotube radii. This is also supported by the measurements of a \( T_c \approx 15 \) K in the 4 Angstrom SWNT by Tang et al.[5]. However, in the limit of large \( N \), \( \Delta_{\text{asympt}}(N) \) remains stable around 1.7 meV and may be interpreted as the binding energy of the \( W = 0 \) pair in an optimally doped graphite sheet. By a rough order of magnitude estimate, we may say that the superconducting critical temperature predicted by our approach at \( \epsilon_F = 1 \) eV (which corresponds to a number of electrons per graphite atom of 1.25) is \( T_c \approx \Delta_{\text{asympt}}(\infty) \approx 10 \div 20 \) K. The order of magnitude of the computed pair binding energy agrees with experiment[36].

### 6 Conclusions

For \( (N, N) \) armchair nanotubes, the effective interaction \( W_{\text{eff}} \) of Eq.(19) arises from the on-site electronic repulsion. Inserting \( W_{\text{eff}} \) in Eq.(20) leads to pairing and the binding energy is in the meV range. Despite the heuristic nature of the Hubbard Model, it is gratifying that the order of magnitude of the pair binding energy agrees well with experiment[5]. Furthermore, the decrease of the binding energy with \( N \) is suggested by recent measurements on nanotubes with diameter of few Angstrom[5]. The analytical approximation has been validated with high accuracy by comparison with exact-diagonalization data in the case \( N = 1 \).

The paired state we have obtained here is essentially two-dimensional, that is the transverse direction is crucial to have a non-Abelian symmetry group and hence \( W = 0 \) pairs away from half filling. It has been argued that weakly doped nanotubes are Luttinger liquids down to milli-Kelvin temperatures[3][37]. This opens up an interesting possibility. In
nanotubes, two distinct superconducting order parameters could appear in the phase diagram: in doped nanotubes, pairing occurs by the $W = 0$ scenario, while close to half-filling there could be another one due to a breakdown of the Luttinger liquid[38].

Carbon nanotubes and high-$T_c$ Cuprates are widely different for composition and physical properties. However, symmetry arguments based on the above $W = 0$ theorem suggest that, despite the obvious differences, part of the story must be the same.

The present treatment based on a Hubbard model ignores vibrations from the outset and one should seek some way to include them in the model with the resulting possibility that static or dynamic Jahn-Teller distortions modify the problem. Here we reported some preliminary results obtained on a simple square lattice and compared to exact diagonalization data on a tiny (5-site) system. The results indicate that the situation is complex, as can be expected in an enlarged parameter space. However, exact solutions confirm that the $W = 0$ pairing survives and also gains stability, as opposed to those findings where simpler approximations would predict distortion and pair breaking. This is because the neglect of the excited states underestimates the flexibility of the pair ad its ability to ride the vibrations.

References


On the Pairing Mechanism in Doped Armchair Carbon Nanotubes


